BINDER FREE ELECTRODE FOR EFFICACIOUS SUPERCAPACITORS: ROLE OF VARIOUS METAL OXIDE NANOCOMPOSITES COMBINED WITH REDOX ADDITIVE ELECTROLYTE

A SYNOPSIS

Submitted by

S. ARUNPANDIYAN

(Reg. No. 201815138)

in partial fulfilment for the award of the degree

of

DOCTOR OF PHILOSOPHY

DEPARTMENT OF PHYSICS

SCHOOL OF ADVANCED SCIENCES

KALASALINGAM ACADEMY OF RESEARCH AND EDUCATION

(DEEMED TO BE UNIVERSITY)

ANAND NAGAR, KRISHNANKOIL – 626 126

TAMILNADU, INDIA

OCTOBER 2022

1. INTRODUCTION

The need for highly efficient energy storage devices was increased with modernization and automation. Especially, the automobile industry has vital importance to develop energy storage devices in precise, smart, lightweight, and viable due to the transformation of current combustion vehicles to all-electric. But the key challenges in these transformations were the limited abundance and toxicity of lithium used in Li-ion batteries, which were widely used in most electric vehicles. To accomplish this, research interest in supercapacitors (SCs) was tremendously increased. Still, the supercapacitors were lacking in many things in order to meet the requirement for large-scale commercial applications [1–4].

The conventional electric double-layer capacitors were generally made-up of carbon derivatives, such as activated carbon, graphene, carbon nanotubes, carbon aerogels, etc. They usually possessed greater power density and cycling stability over the aqueous electrolytic environment [5–6]. But the poor energy density with short operating time and high cost were the major issues in commercial usage. So, the recent research interests were extended to metal oxide-based pseudocapacitors due to their enhanced energy density and superior specific capacitance values. To acquire high performances, the preparation of metal oxide nanostructures with high surface area and porosity were the key components. Even after achieving high surface area and porosity, the major challenge was the fabrication of the working electrode with the material's original surface area and porosity. Because, the polymeric binders used in the conventional electrode fabrication techniques will reduce the active surface area, porosity, and charge transport phenomenon of the electrode materials. It suggested the significance to develop binder-free electrodes for supercapacitor applications. Recently, different approaches were carried out to fabricate binder-free electrodes for high-performance and flexible supercapacitors. Among them, the hydrothermal approach was the most effective and feasible one. Binder-free working electrodes were fabricated on various substrates, like Ni foam, carbon cloths, carbon sheets, carbon fiber electrodes, Mo foil, Ni foil, etc. Among them, Ni foam substrates received unique attention due to their highly reported supercapacitor performance [7–12].

Supercapacitor device performances not only rely on the electrode performances, but the electrolytes also hold some importance. Generally, electrolytes were used as the charge transfer medium during the electrochemical processes. But, the conventional aqueous and organic electrolytes fail to support the performance and stability improvement of the supercapacitor devices. It suggested the necessity of a newly upgraded electrolyte, which not only acted as the charge transfer medium but also acted as the active medium of the supercapacitor devices. To accomplish this, the recent developments in supercapacitor device performance have attained some popularity in the sense of redox additive-based electrolytes[13–18]. Usually, researchers concentrated on some redox additives, like $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, KI, hydroquinone, etc., for the performance enhancement of conventional electrolytes. Among all of them, 0.2 M $K_4[Fe(CN)_6]$ added 3 M KOH redox additive electrolyte received unique attention due to the improvement in energy/power densities, cycling stability, specific capacitance, etc.

2. LITERATURE SURVEY

Manufacturing methods of SCs electrode material play a major role in their performances. Thermal stability, high specific surface area, chemical resistance, high electrical conductivity, acceptable chemical stability, and good surface wettability were the required characteristics for the SC electrodes. Also, they should be low-cost and ecologically friendly, as well as capable of converting Faradaic charge to enhanced capacity. In reality, the specific capacitance factor was influenced not only by the surface area, but also by other important factors such as simple morphological modification, pore size distributions, pore shape, pore diameters, and their availability for the electrolyte. Two more crucial requirements were needed for designing an SC device, such as,

1. Enhancement of electrochemically active sites by the proper selection of active materials with more surface area and
2. Modification of the particle sizes and porous structure of the electrode material to make them suitable candidates for the facilitation of electrolyte ion transportation

Smaller pores in the electrode material result in larger capacitance and consequently leads to higher energy density values. At the same time, smaller pore size enhanced the equivalent series resistance (ESR) values, and hence, it lowers the power density. As the

result, the application of the electrode material influences the selection of the material. For example, for applications requiring higher energy density, electrode materials should have larger holes, whereas the applications that required higher peak currents, electrode materials ought to have smaller pores. Moreover, a good size diversity can help with endurance, which was an indicator of a high-power density in the SC devices. The electrode material's effective utilization of micro/mesopores can offer rapid mass and ion transport over a continuous channel, which improves electrolyte accessibility and makes the material suitable for SC applications. Three different types of materials, such as conducting polymers (CPs), metal oxide-based materials, and carbonaceous compounds were used as the electrode materials.

The preparation of the aforementioned porous structured electrode materials itself had many difficulties. Utilization of the total active surface area and pores available in electrode materials on the surface of the working electrode possessed a major drawback. The binders used in the fabrication process and the fabrication techniques reduce the active surface area and pores, which were available on the electrode's surfaces. To overcome these issues, various attempts were made by the researchers to fabricate the working electrodes without the binders.

L.-Q. Fan et al fabricated $CuCo_2S_4$ nanosheet arrays on Ni foam through the hydrothermal approach [19]. The thin interconnected nanosheets of $CuCo_2S_4$ arrays with a thickness of about 10 nm were prepared through this approach. The fabricated binder-free electrode possessed the maximum of 3132.7 Fg^{-1} specific capacitance at 1 Ag^{-1} of current density. Also, the asymmetric supercapacitor fabricated using the binder-free electrode as the positive electrode and activated carbon as the negative electrode, delivered an energy density of 46.1 W h kg^{-1} at the power density value of 991.6 W kg^{-1}. The fabricated device exhibited promising rate capability and cycling stability values.

Karimi et al fabricated a novel PPy/FeCoS-rGO ternary system on Ni foam as the binder-free electrode through a two-step electro-deposition approach [20]. The PPy/FeCoS-rGO/NF electrode possessed the 3178 Fg^{-1} of specific capacitance at 2 Ag^{-1} of current density, and a good rate capability (70% capacitance retention up to 30 A g^{-1}). The asymmetric supercapacitor device based on PPy/FeCoS-rGO/NF (positive electrode)

and rGO/NF (negative electrode) delivered a high specific capacitance of 94 F g^{-1} at 1 A g^{-1} current density. The constructed ASC device possessed, 28.3 W h kg^{-1} of energy density at 810 W kg^{-1} power density with 97.5% retention up to 2500 cycles.

Agudosi et al proposed nickel oxide deposited graphene as a binder-free electrode (G-NiO) through the vapor deposition method [7]. The G-NiO binder-free electrode exhibited a maximum of 243 Cg^{-1} specific capacity at 3 mVs^{-1} of scan rate in a three-electrode system. Then, they prepared a two-electrode system with G-NiO//AC as the supercapattery device with 1.4 V operating potential. The assembled supercapattery device possessed 47.3 W h kg^{-1} of energy density at 140 W kg^{-1} of power density. Also, 98.7% capacitance retention up to 5,000 charge-discharge cycles was achieved.

The literature suggested the feasibility of binder-free electrodes in supercapacitor electrode fabrications. Also, it could possibly improve the electrochemical performances, such as specific capacitance, energy/power densities, and cyclic stability by the enhanced active surface area of the electrode material, which reduced the necessity for polymeric binders. Removal of polymeric binders possibly reduced the cost and improved the charge transfer characteristics. Especially growth of nanostructured porous materials over Ni foam substrate through the hydrothermal method attracted greater attention according to the literature.

As electrode materials for high-performance supercapacitor applications, rare-earth metal oxides received a huge attraction in recent times. The trivalent and divalent ions of rare earth have particularly intriguing optical and magnetic characteristics because of the imperfect 4f shell. According to the reports, rare earth ions revealed superior cyclic stability and specific capacitance values. Especially, CeO_2 was anticipated as a suitable electrode material for supercapacitors, because of its abundance on Earth, dynamic redox pair, and environmentally favorable qualities. Due to the direct and quick transition between the two well-known redox states, Ce (III) and Ce (IV), it acted as the novel and difficult electrode material for supercapacitors. Only a few reports discussed the use of cerium oxide's pseudocapacitive qualities. The architecture and redox durability of cerium oxide had undergone substantial improvements.

Jeyaranjan et al reported the significance of nano cerium oxide (CeO_2) prepared in different morphologies (nanoparticles, nanorods, nanocubes) via the one-pot hydrothermal method [21]. The electrochemical performances were evaluated by cyclic voltammetry and galvanostatic charge-discharge techniques. Although CeO_2 was a potential supercapacitor material, the impact of topology on charge storage capacity was still unknown. Three distinct topologies, nanorods, cubes, and particles, were prepared by a one-step hydrothermal procedure to assess the topology effect. Each topology possessed different specific capacitance values based on its active surface area and the amount of oxygen exposure in the active surface sites. In all three topologies, the CeO_2 nanorods revealed a high specific capacitance value of 162.47 F g^{-1}, derived from its high active surface area and high reactivity by (110) and (100) crystal plane exposures.

The electrochemical capabilities of supercapacitors were enhanced using a variety of techniques. One of the most promising approaches used to enhance redox capabilities and performance was the incorporation of redox additives (or redox mediators) into conventional aqueous electrolytes. Recent literature suggested that the addition of redox additives in aqueous electrolytes improved the electrochemical performances by increasing the charge storage capacity through redox transformations.

Senthilkumar et al briefed on the significance of redox-mediated electrolytes in energy storage devices [22]. In addition to redox additives or mediators into the electrolytes, the performances of the SCs were increased via redox processes at the electrode-electrolyte interfaces. The key benefit of this combination was its ease of use and safety, as well as its cost-effectiveness when compared to the preparation of various active electrode materials. As a result, the selection of acceptable redox additives or entities in near future becomes the flashpoint in the field of SCs.

Ramachandran et al synthesized cerium metal-organic framework-based composites (Ce-MOF/GO and Ce-MOF/CNT) through the wet chemical approach [23]. The electrochemical performances of the prepared composites were studied and compared in 3 M KOH and 3 M KOH + 0.2 M $K_3Fe(CN)_6$ electrolytes. Prepared Ce-MOF/GO composite showed improved electrochemical performance in 0.2 M $K_3Fe(CN)_6$ redox additives added 3 M KOH, with a maximal specific capacitance of 2221.2 Fg^{-1} and an

energy density of 111.05 W h kg^{-1} at a current density of 1 Ag^{-1}. The wide mesoporous structure of Ce-MOF/GO and the presence of oxygen functional groups in the electrode/electrolyte interface might aid ion transport.

The aforementioned literature suggested that the 0.2 M $K_3Fe(CN)_6$ added 3 M KOH redox additive electrolyte was one of the most viable and suitable redox additive electrolytes in supercapacitor applications. Redox additive electrolytes also improved the cycling stability along with energy density, power density, and specific capacitance values of the supercapacitors. This suggested the significance of 0.2 M $K_3Fe(CN)_6$ added 3 M KOH redox additive electrolytes in real-time applications.

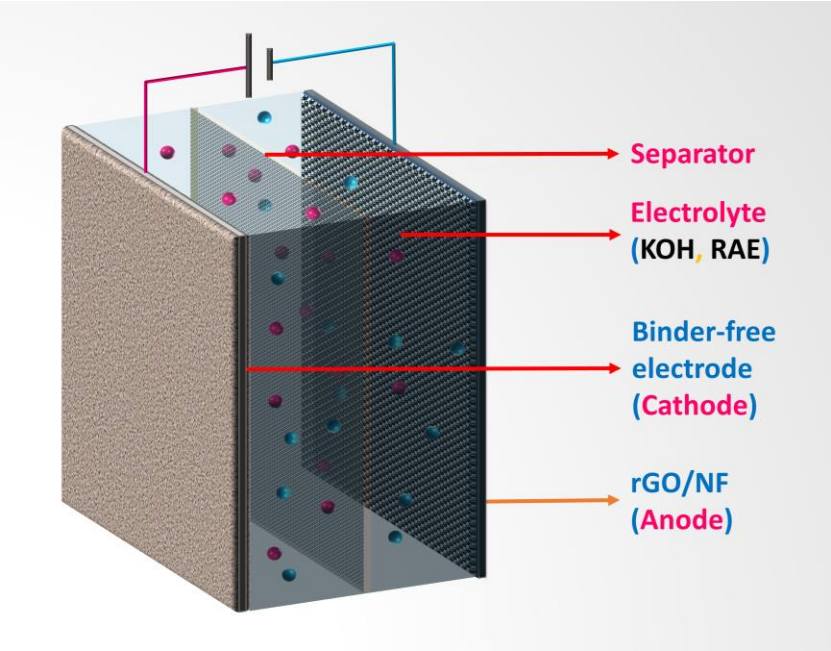

Figure 1. The basic structure of the proposed supercapacitor device containing a binder-free electrode and redox additive electrolyte combination

According to the literature, the performances of supercapacitors can be enhanced by two different approaches, such as, (1). Incorporation of binder-free electrodes, which effectively utilizes the available active surface areas of the electrode materials and, (2) Utilization of redox additives, which was used to induce the redox reactions within the electrolyte by redox additives. The combined effect of binder-free electrodes and redox additive electrolytes may lead to achieving the maximum possible electrochemical

performances [Figure 1]. Also, the above combination was used to improve the long-term cycling stability, charge transfer capabilities, and balanced enhancement in energy and power densities of the supercapacitors.

Ganesh et al reported the combined effect of Co_3O_4@nickel foam binder-free electrodes and redox additive electrolytes with two different Co_3O_4 structures (plate-like, p-Co_3O_4, and grass-like, g-Co_3O_4) [24]. The electrochemical performance of the electrodes was tested using a redox-additive electrolyte (RAE). The homogeneously grown grass-like nanostructure (g-Co_3O_4) exhibited superior electrochemical performance than the plate-like structure (p-Co_3O_4) in a 3 M KOH electrolyte. In addition, the electrochemical performance of g-Co_3O_4 was improved using an RAE in a 3 M KOH solution. Remarkably, the specific capacitance of g-Co_3O_4 (1560 F g^{-1}) was increased to 6580 F g^{-1}, approximately 4-fold just by varying the RAE concentration in KOH. Carbon nano-onion (CNO) in the form of multi-layer fullerene was introduced as the negative electrode material. Owing to the more favorable morphology and properties of CNO, such as hexahedral structure, small diameter, high electrical conductivity, and relatively easy aqueous media dispersion than activated carbon and graphene, the as-fabricated asymmetric Co_3O_4//CNO supercapacitor delivered a high energy and power density and density values of 42.5 Wh kg^{-1} and 12.8 kW kg^{-1} respectively.

3. Objective

Supercapacitors received considerable attention in the current era, yet they needed more improvements in a variety of aspects, such as cost, raw materials abundance, and energy density. To facilitate these shortcomings, the researchers are attempting a range of new techniques. One among them was the binder-free electrode, which can be easily fabricated by a one-pot hydrothermal technique to preserve the nanostructured materials with their original surface area. This could improve the overall electrochemical characteristics of the system by eliminating the demerits of conventional supercapacitor electrodes. Conventional electrodes were fabricated through the Doctor blade technique by using polymeric binders, which affected the electrode material's surface area and charge transfer characteristics. The other technique predominantly anticipated was the use of redox additive-based electrolytes in supercapacitor devices. These redox additive-based

electrolytes were capable of improving the electrochemical performances of the system without any complicated intricacies.

Exhilarated by preceding recitals, different metal oxides, mixed metal oxides, and rGO-doped mixed metal oxide nanostructures can be deposited over the Nickel Foam (NF) substrate through a one-pot hydrothermal method for ameliorated electrochemical performances. The literature amply demonstrates that cerium oxide-based materials were suitable for potassium ferrocyanide-based redox additive electrolytes. Because their Ce^{3+}/Ce^{4+} and $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ states precisely match one other to support each other by providing electrons to improvise the redox reactions.

The objective of this work was to study the role of various metal oxides and 0.2 M $K_4[Fe(CN)_6]$ based redox additive electrolytes on the supercapacitor performance of metal oxide (CeO_2) based binder-free electrodes. It will be accomplished through the following steps,

- Investigations on the practicality and feasibility of the binder-free electrodes based on metal oxide nanocomposites (ZnO/NiO:rGO)
- Optimizing the feasibility of $K_4[Fe(CN)_6]$ mixed KOH-based redox additive electrolyte with CeO_2-based nanocomposites (ZnO/CeO_2 & MnO_2/CeO_2)
- Investigations of the combined effect of redox additive electrolyte and CeO_2-based binder-free electrodes
- Fabrication of various transition metal oxide loaded CeO_2 nanocomposites based binder-free electrodes and their electrochemical performances under 0.2 M $K_4[Fe(CN)_6]$ incorporated 3 M KOH redox additive electrolyte

4. Research Problem

Modern gadgets and their transformations required modern upgrades in energy storage devices. Conventional energy storage devices possessed the following problems that should be accounted for and rectified.

- Conventional Li-ion batteries utilize less abundant, high cost and hazardous lithium minerals as the core raw material

- The commercial batteries exhibited poor power density and life span compared to supercapacitors, which should be improved for real-time applications
- The conventional doctor blade technique used for the fabrication of working electrodes utilized various polymeric binders such as PVDF, PTFE, Nafion, etc., which reduces the active surface area pores for the diffusion of electrolyte
- Conventional electrolytes acted as the charge transport medium only, which reduced the overall performance of the system
- Modern supercapacitors required highly active binder-free electrodes and electrolytes for better performances

5. Organization of Thesis

Energy storage devices play a crucial role in the modern world as the interface between energy production and applications. Since conventional energy sources were going to be depleted soon, research on alternative energy sources and efficient energy storage systems was drastically increased. Since conventional energy storage devices, such as batteries, and capacitors, were related to environmental concerns and efficiency, alternative energy storage devices with the advances of conventional batteries and capacitors were required for modern applications. However, the current advances and techniques used in conventional energy storage technology were, high-cost, tedious to process, and difficult to replicate. All these demerits were overcome by the introduction of high-performance supercapacitors. But the performance and applications of supercapacitors were limited by the cost, active surface area, and stability of the working electrodes and the lacking of redox reactions on the electrolytes. To overcome these demerits, supercapacitor devices with binder-free electrodes and redox additive electrolyte combinations were proposed. Since the proposed binder-free electrodes were made up of simple metal oxides and composites, the difficulties (toxicity, less abundance, and cost) raised by the conventional electrodes were rectified. Also, the incorporation of redox additive-based electrolytes enhanced the possible redox reactions within the electrolyte, which improved the overall storage ability of the fabricated supercapacitor devices. This thesis discusses the possible ways to improve the performance of supercapacitor devices through the incorporation of binder-free electrodes and redox additive electrolyte

combinations. The objectives of the proposed work were completed in different steps and reported in eight different chapters as follows.

Chapter 1 discusses the introduction and background of different electrochemical energy storage technologies. A short overview of the classification of various electrochemical energy storage technologies, such as capacitors, batteries, fuel cells, redox flow batteries, and supercapacitors was discussed. Furthermore, a brief overview, classifications, and working mechanism of supercapacitor technology were described. The role of different components in the performance of supercapacitor devices was briefed. Most importantly, the challenges of supercapacitors in commercial applications and the solution to solve the issues were deliberated. Also, the current and future applications of supercapacitor applications and their scope *vs.* span were clearly illustrated. Based on the gap identified in the current electrode material fabrication techniques and the role of electrolytes, the necessity of binder-free electrodes and redox additive electrolytes was specified.

Chapter 2 describes the literature review of the current research work. The key characteristic requirements of a supercapacitor to meet the current trend were listed precisely. Different types of materials utilized for electrode fabrication were elaborately reviewed. Based on the literature, the key aspects and the significance of binder-free electrodes were identified. The role of conventional electrolytes and their types used in the supercapacitors were reviewed. The steps involved in the performance enhancement of conventional electrolytes and the significance of redox additive-based electrolytes were discussed. The compatibility and performance of binder-free electrode and redox additive electrolytes combination and their significance were provided. Finally, the scope of the current research work was listed precisely.

Chapter 3 deals with the experimental part of the research work. A detailed list of reagents and instruments used in the research work was illustrated. Also, the fundamentals and instrumentations of some characterization techniques, such as X-ray diffraction analysis (XRD), Fourier Transform Infra-Red (FT-IR) spectroscopy (XPS), Scanning Electron Microscopy (SEM), and High-Resolution Transmission Electron Microscopy (HR-TEM), which were utilized for the characterization of the proposed materials were

described. Furthermore, the techniques involved in electrochemical analysis (Cyclic Voltammetry - CV, Galvanostatic Charge-Discharge – GCD, Electrochemical Impedance Spectroscopy - EIS), their fundamentals, functions, and roles were briefly explained.

Chapter 4 deals with the significance of the ZnO/NiO:rGO coated Ni foam binder-free electrode in supercapacitor applications. ZnO/NiO:rGO nanocomposites and ZnO/NiO:rGO nanocomposite-coated Ni foam binder-free electrodes were fabricated through the hydrothermal method. Prepared nanocomposites were analytically characterized by XRD, FT-IR, FT-Raman, SEM, and HR-TEM analyses to examine their physiochemical characteristics. The electrochemical characteristics of the fabricated binder-free electrodes were tested under 1 M KOH electrolyte, and it exhibited a maximum of 622.3 Fg^{-1} specific capacitance at 1 Ag^{-1}. An asymmetrical type supercapacitor was fabricated using ZnO/NiO:rGO nanocomposite coated Ni foam binder-free electrode as the cathode and rGO coated Ni foam as the anode. The fabricated device possessed a maximum of 2460 W kg^{-1} and 16.7 W h kg^{-1} power and energy densities respectively. The fabricated device showed 85.7% of electrochemical retention after 10,000 GCD cycles and it was one of the key advantages for long-term application.

Chapter 5(a) deals with the enhanced electrochemical performances of ZnO/CeO_2 nanocomposite under redox additive electrolyte. It describes the compatibility studies on the incorporation of redox additives in conventional electrolytes and their performance against ZnO/CeO_2-modified working electrodes. ZnO/CeO_2 nanocomposites were prepared through the simple chemical precipitation method and the prepared nanocomposites were calcinated at 750 °C. The structural, functional, and surface characteristics of the calcinated samples were studied by XRD, FT-IR, and SEM analyses, respectively. ZnO/CeO_2 nanocomposite-modified Ni foil was fabricated using the Doctor Blade technique and used as the working electrode. To examine the performance of redox additive electrolyte, the electrochemical performance of ZnO/CeO_2 nanocomposite modified working electrode was tested under pure 3 M KOH and 0.2 M $K_4[Fe(CN)_6]$ redox additive added 3 M KOH aqueous electrolytes. ZnO/CeO_2 nanocomposite modified working electrode revealed better performances under redox additive electrolyte with the specific capacitance value of 1069 Fg^{-1} than conventional KOH electrolyte.

Chapter 5(b) deals with the enhanced supercapacitor performances of CeO_2 nanoparticles decorated hierarchically porous MnO_2 nanorods under redox additive electrolyte. Pure CeO_2 nanoparticles (NPs) and MnO_2 nanorods (NRs) were prepared by a simple hydrothermal technique. Prepared CeO_2 NPs were uniformly coated over the MnO_2 NRs through a facile ultrasonic technique. The uniform distribution of CeO_2 NPs over MnO_2 NRs was analyzed by the scanning electron microscopy technique. Crystalline phases of pure CeO_2, MnO_2, and the formation of CeO_2 NPs decorated MnO_2 NRs were investigated by the XRD analysis. The surface chemical composition and the formation of CeO_2 NPs decorated MnO_2 NRs were examined by the XPS analysis. The electrochemical performances of the prepared sample were studied by using 3 M aqueous KOH and 0.2 M $K_4[Fe(CN)_6]$ added to 3 M KOH electrolytes. CeO_2 nanoparticles decorated MnO_2 nanorods exhibited the superior capacitance of 1058.2 Fg^{-1} under 0.2 M $K_4[Fe(CN)_6]$ added 3 M KOH redox additive-based electrolyte.

Chapter 6 deals with the combined effect of hierarchically porous CeO_2 micro rice-supported Ni foam binder-free electrode and redox additive electrolyte on their electrochemical performances. Herein, a hierarchically porous CeO_2 micro rice was loaded on the Ni foam (NF) surface via a facile hydrothermal approach. The fabricated binder-free electrode exhibited a maximum specific capacitance of 728.3 Fg^{-1} under 3 M KOH electrolyte. Further, the addition of 0.2 M $K_4[Fe(CN)_6]$ in 3 M KOH, improved the specific capacitance values to 2319.5 Fg^{-1}. The drastic improvement in electrochemical performances was achieved by the reversible redox reactions occurring in the electrolyte due to the inclusion of 0.2 M $K_4[Fe(CN)_6]$. The as-prepared binder-free electrode retained 85.3% of its initial capacitance in 3 M KOH, even after 5000 cycles, and in the redox additive electrolyte, the retention was increased to 92.7%. The highest energy and power density values of 39.6 W h kg^{-1} and 550 W kg^{-1}, respectively, were achieved by the combined effect of CeO_2 micro rice-supported Ni foam binder-free electrode and redox additive electrolyte.

Chapter 7 deals with improved electrochemical performances of transition metal oxides loaded CeO_2 ((Co_3O_4, Bi_2O_3, NiO, CuO)/CeO_2) nanocomposite-based binder-free electrode under redox additive electrolyte. The structural, functional, and morphological characteristics of the prepared nanocomposites were investigated by various analytical

techniques. The electrochemical performances of the fabricated binder-free electrodes were initially tested under a 3 M KOH electrolyte. Further, the enhanced electrochemical performances by the addition of 0.2 M $K_4[Fe(CN)_6]$ redox additive into 3 M KOH were investigated and reported. The improved electrochemical characteristics were listed in Table 1.

Table 1. Electrochemical performances of the fabricated TMO/CeO_2@NF and RAE combination

S. No.	Binder free electrode	Specific capacitance from GCD (Fg^{-1})		Energy density ($W\ h\ kg^{-1}$)	Power density ($W\ kg^{-1}$)	Cycling stability (5000 cycles)
		KOH	RAE			
1.	Co_3O_4/CeO_2@NF	650.3	2975	45.2	4320	93.1%
2.	Bi_2O_3/Ce_2O_3@NF	14.5	1460.8	15.1	1440	82.7%
3.	NiO/CeO_2@NF	77.3	235.7	37.4	1440	96.8%
4.	CuO/CeO_2@NF	69.8	1210	9.7	3840	88.3%

Finally, chapter 8 confers the overall summary of all the research works described in the dissertation. In detail, the significance of binder-free electrodes, redox additive electrolytes, and their combined effect was clearly illustrated. Furthermore, the effects of various metal oxides loaded on the CeO_2 nanoparticles and their electrochemical performances were clearly reported. Through the knowledge acquired from the dissertation, an effective future work plan to attain real-time application was also enlisted.

6. References

1. Poonam, K. Sharma, A. Arora, and S. K. Tripathi, Review of supercapacitors: Materials and devices. *Journal of Energy Storage*, **21** (2019), 801–825.

2. L. Zhang, X. Hu, Z. Wang, F. Sun, and D. G. Dorrell, A review of supercapacitor modeling, estimation, and applications: A control/management perspective. *Renewable and Sustainable Energy Reviews*, **81** (2018), 1868–1878.

3. J. Zhao, Y. Tian, A. Liu, L. Song, and Z. Zhao, The NiO electrode materials in electrochemical capacitor: A review. *Materials Science in Semiconductor Processing*, **96** (2019), 78–90.

4. S. Najib and E. Erdem, Current progress achieved in novel materials for supercapacitor electrodes: Mini review. *Nanoscale Advances*, **1** (2019), 2817–2827.

5. R. Dubey and V. Guruviah, Review of carbon-based electrode materials for supercapacitor energy storage. *Ionics*, **25** (2019), 1419–1445.

6. S. Z. Hussain, M. Ihrar, S. B. Hussain, W. C. Oh, and K. Ullah, A review on graphene-based transition metal oxide composites and its application towards supercapacitor electrodes. *SN Applied Sciences*, **2** (2020), 764.

7. E. S. Agudosi, E. C. Abdullah, A. Numan, N. M. Mubarak, S. R. Aid, R. Benages-Vilau, P. Gómez-Romero, M. Khalid, and N. Omar, Fabrication of 3D binder-free graphene NiO electrode for highly stable supercapattery. *Scientific Reports*, **10** (2020), 11214.

8. G. K. Veerasubramani, K. Krishnamoorthy, and S. J. Kim, Improved electrochemical performances of binder-free $CoMoO_4$ nanoplate arrays@Ni foam electrode using redox additive electrolyte. *Journal of Power Sources*, **306** (2016), 378–386.

9. H. Jiang, X. Ye, Y. Zhu, L. Wang, P. Zhao, Z. Yue, J. Xie, Z. Wan, and C. Jia, Toward high-rate supercapacitor: Preparation of hierarchical porous carbon binder-free electrode with controllable texture. *Applied Surface Science*, **470** (2019), 573–580.

10. T. Lavanya and S. Ramaprabhu, Copper nanoparticles incorporated porous carbon nanofibers as a freestanding binder-free electrode for symmetric supercapacitor with enhanced electrochemical performance. *Materials Research Express*, **6** (2019), 105005.

11. N. Yu, L. Zou, C. Li, and K. Guo, In-situ growth of binder-free hierarchical carbon coated $CoSe_2$ as a high performance lithium ion battery anode. *Applied Surface Science*, **483** (2019), 85–90.

12. Y. Abbas, S. Yun, M. S. Javed, J. Chen, M. F. Tahir, Z. Wang, C. Yang, A. Arshad, and S. Hussain, Anchoring 2D $NiMoO_4$ nano-plates on flexible carbon cloth as a binder-free electrode for efficient energy storage devices. *Ceramics International*, **46** (2020), 4470–4476.

13. V. T. Nguyen and J.-M. Ting, A Redox-Additive Electrolyte and Nanostructured Electrode for Enhanced Supercapacitor Energy Density. *ACS Sustainable Chemistry & Engineering*, **8** (2020), 18023–18033.

14. J. Lee, P. Srimuk, S. Fleischmann, X. Su, T. A. Hatton, and V. Presser, Redox-electrolytes for non-flow electrochemical energy storage: A critical review and best practice. *Progress in Materials Science*, **101** (2019), 46–89.

15. L.-Q. Fan, Q.-M. Tu, C.-L. Geng, Y.-L. Wang, S.-J. Sun, Y.-F. Huang, and J.-H. Wu, Improved redox-active ionic liquid-based ionogel electrolyte by introducing carbon nanotubes for application in all-solid-state supercapacitors. *International Journal of Hydrogen Energy*, **45** (2020), 17131–17139.

16. D. Jain, J. Kanungo, and S. K. Tripathi, Enhanced performance of ultracapacitors using redox additive-based electrolytes. *Applied Physics A*, **124** (2018), 397.

17. S. Sundriyal, V. Shrivastav, M. Sharma, S. Mishra, and A. Deep, Redox Additive Electrolyte Study of Mn–MOF Electrode for Supercapacitor Applications. *Chemistry Select*, **4** (2019), 2585–2592.

18. W. Qin, N. Zhou, C. Wu, M. Xie, H. Sun, Y. Guo, and L. Pan, Mini-Review on the Redox Additives in Aqueous Electrolyte for High Performance Supercapacitors. *ACS Omega*, **5** (2020), 3801–3808.

19. L. Q. Fan, F. Pan, Q. M. Tu, Y. Gu, J. L. Huang, Y. F. Huang, and J. H. Wu, Synthesis of $CuCo_2S_4$ nanosheet arrays on Ni foam as binder-free electrode for asymmetric supercapacitor. *International Journal of Hydrogen Energy*, **43** (2018), 23372–23381.

20. A. Karimi, I. Kazeminezhad, L. Naderi, and S. Shahrokhian, Construction of a Ternary Nanocomposite, Polypyrrole/Fe–Co Sulfide-Reduced Graphene Oxide/Nickel Foam, as a Novel Binder-Free Electrode for High-Performance Asymmetric Supercapacitors. *The Journal of Physical Chemistry C*, **124** (2020), 4393–4407.

21. A. Jeyaranjan, T. S. Sakthivel, M. Molinari, D. C. Sayle, and S. Seal, Morphology and Crystal Planes Effects on Supercapacitance of CeO_2 Nanostructures: Electrochemical and Molecular Dynamics Studies. *Particle & Particle Systems Characterization*, **35** (2018), 1800176.

22. S. T. Senthilkumar, R. K. Selvan, and J. S. Melo, Redox additive/active electrolytes: a novel approach to enhance the performance of supercapacitors. *Journal of Materials Chemistry A*, **1** (2013), 12386–12394.

23. R. Ramachandran, W. Xuan, C. Zhao, X. Leng, D. Sun, D. Luo, and F. Wang, Enhanced electrochemical properties of cerium metal–organic framework based composite electrodes for high-performance supercapacitor application. *RSC Advances*, **8** (2018), 3462–3469.

24. G. Dhakal, D. Mohapatra, T. L. Tamang, M. Lee, Y. R. Lee, and J. J. Shim, Redox-additive electrolyte–driven enhancement of the electrochemical energy storage performance of asymmetric Co_3O_4//carbon nano-onions supercapacitors. *Energy*, **218** (2021), 119436.

7. List of Publications

[1] S. Arunpandiyan, S. Bharathi, A. Pandikumar, S. Ezhil Arasi, and A. Arivarasan, Structural Analysis and Redox Additive Electrolyte Based Supercapacitor Performance of ZnO/CeO_2 Nanocomposite, *Materials Science in Semiconductor Processing*, **106** (2020), 104765.

[2] S. Arunpandiyan, S. Vinoth, A. Pandikumar, A. Raja, and A. Arivarasan, Decoration of CeO_2 Nanoparticles on Hierarchically Porous MnO_2 Nanorods and Enhancement of Supercapacitor Performance by Redox Additive Electrolyte, *Journal of Alloys and Compounds*, **861** (2021), 158456.

[3] S. Arunpandiyan, A. Raja, S. Vinoth, A. Pandikumar, and A. Arivarasan, Hierarchical Porous CeO_2 Micro Rice-Supported Ni Foam Binder-Free Electrode and its Enhanced Pseudocapacitor Performance by a Redox Additive Electrolyte, *New Journal of Chemistry*, **45** (29) (2021), 12808–12817.

[4] S. Arunpandiyan, A. Raja, S. Bharathi, and A. Arivarasan, Fabrication of ZnO/NiO:rGO Coated Ni Foam Binder-Free Electrode via Hydrothermal Method for Supercapacitor Application, *Journal of Alloys and Compounds*, **883** (2021), 160791.